SUPPORTED CATALYST COMPOSITIONS HAVING IMPROVED FLOW PROPERTIES AND PREPARATION THEREOF

FIELD

[0001] The present disclosure relates to supported catalyst compositions having improved flow properties, methods for their preparation and to their use in processes for polymerizing olefins. In particular, the disclosure relates to supported catalyst compositions comprising methylalumoxane activators and metallocene type catalyst compounds and/or conventional-type transition metal catalyst compounds which have improved flow properties.

BACKGROUND

[0002] Metallocene type catalysts are widely used to produce polyolefin polymers such as polyethylene polymers. They have provided efficient processes and a variety of new and improved polymers. While there are many advantages to using metallocene catalysts in olefin polymerizations, there remain significant challenges. For example, metallocene catalysts, in particular supported metallocene catalysts, often have poor flowability, and the supported catalyst particles tend to adhere to surfaces or form agglomerates. Adding other reagents to the supported catalyst composition, such as commonly known antifouling agents or continuity additives/aids may compound the flowability issue. This causes practical problems in storing, transporting, and then delivering the dry supported catalyst composition into a polymerization reactor.

[0003] Supported catalyst compositions may also have poor polymerization reactor operability, often caused by uneven distribution of catalyst active sites within the porous particles of the support. In particular, 'hot-spots' on the external surface of the support may result from such poor distribution, negatively affecting reactor operability.

[0004] It would be desirable to provide a supported catalyst composition for olefin polymerization that has good flowability and that may provide enhanced reactor operability.

SUMMARY

[0005] There is provided a supported catalyst composition for olefin polymerization comprising one or more particulate supports, one or more catalyst compounds, and one or more activator compounds, wherein the supported catalyst composition has a macro pore volume of less than or equal to 1.23 cm^3/g. The macro pore volume may be determined using mercury intrusion porosimetry according to ISO 15901-1.

[0005a] In one aspect, there is provided a supported olefin polymerization catalyst composition comprising one or more particulate supports, one or more catalyst compounds, a continuity

additive and one or more activator compounds, wherein the supported catalyst composition is formed by drying a suspension including the one or more particulate supports, the one or more catalyst compounds, the continuity additive, the one or more activator compounds, and a diluent and has a macro pore volume, as determined by ISO 15901-1, of less than or equal to 1.23 cm^3/g but greater than or equal to 0.8 cm^3/g, wherein the drying is performed at a temperature of less than or equal to 65°C and at a pressure that is less than or equal to 8 psia; and wherein one or more catalyst compounds are metallocene type catalyst compounds and/ or conventional-type transition metal catalyst compounds.

[0006] In some embodiments macro pore volume may be characterized as the total volume of pores having a pore width greater than 0.05 μm.

b) drying the suspension to form the supported catalyst composition;

wherein step b) is performed at a pressure which is greater than or equal to the vapor pressure of the one or more diluents.

[0020a] In another aspect, there is provided a method for producing a supported olefin polymerization catalyst composition comprising the steps of:

a) forming a suspension comprising one or more particulate supports, one or more catalyst compounds, a continuity additive, and one or more activator compounds in one or more liquid diluents; and

b) drying the suspension to form the supported catalyst composition;

wherein the supported catalyst composition has a macro pore volume, as determined by ISO 15901-1, of less than or equal to 1.23 cm^3/g but greater than or equal to 0.8 cm^3/g and step b) is performed at a temperature of less than or equal to 65°C and at a pressure which is greater than or equal to the vapor pressure of the one or more diluents, wherein the pressure is less than or equal to 8 psia; and wherein one or more catalyst compounds are metallocene type catalyst compounds and/ or conventional-type transition metal catalyst compounds.

[0021] The suspension may comprise one liquid diluent. The liquid diluent may comprise an aliphatic or aromatic hydrocarbon. The liquid diluent may comprise toluene.

[0022] The drying may be performed under conditions wherein substantially no gas bubbles of diluent are formed within the pores of the support particles.

[0023] The drying may be performed at a temperature of less than or equal to 70°C, or less than or equal to 65°C, or less than or equal to 60°C, or less than or equal to 55°C, or less than or equal to 50°C, or less than or equal to 45°C.

[0024] The drying may be performed at a pressure of less than or equal to 2 psia, or less than or equal to 3 psia, or less than or equal to 4 psia, or less than or equal to 5 psia, or less than or equal to 6 psia, or less than or equal to 8 psia.

[0025] The supported catalyst composition formed by the hereinbefore disclosed method may have a macro pore volume of less than or equal to 1.23 cm^3/g. The macro pore volume may be determined using mercury intrusion porosimetry according to ISO 15901-1.

[0026] The supported catalyst composition formed by the hereinbefore disclosed method may have a macro pore volume of less than or equal to 1.20 cm^3/g, or less than or equal to 1.10 cm^3/g, or less than or equal to 1.00 cm^3/g or less than or equal to 0.9 cm^3/g.

[0027] The supported catalyst composition formed by the hereinbefore disclosed method may have an average macro pore width of less than or equal to 5 μm.

[0028] The supported catalyst composition formed by the hereinbefore disclosed method may have an average macro pore width of less than or equal to 3 μm, or less than or equal to 2 μm, or less than or equal to 1 μm, or less than or equal to 0.5 μm.

[0029] The supported catalyst composition formed by the hereinbefore disclosed method may have a tapped bulk density of greater than or equal to 0.30 g/cm^3, or greater than or equal to 0.35 g/cm^3, or greater than or equal to 0.40 g/cm^3 or greater than or equal to 0.45 g/cm^3.

[0030] The particulate support may be a particulate Group 2, 3, 4, 5, 13 and 14 oxide or chloride. The particulate support may be a particulate silica. The particulate support may be dehydrated at an elevated temperature.

[0031] The particulate support may have an average particle size in the range of from about 0.1 to about 500 μm, or from about 1 to about 200 μm, or from about 1 to about 50 μm, or from about 5 to about 50 μm.

[0032] The one or more activator compounds may be an organometallic compound. The one or more activator compounds may be an alumoxane or a neutral or ionic stoichiometric activator. The one or more activator compounds may be methylalumoxane or modified methylalumoxane.

[0033] The supported catalyst composition formed by the hereinbefore disclosed method may have a ratio of Al/Si on the external surface area of the support to Al/Si on the internal surface area of the support of less than or equal to 3.0, or less than or equal to 2.5.

[0034] The one or more catalyst compounds may comprise a titanium, a zirconium, or a hafnium atom. The supported catalyst composition may comprise two or more catalyst compounds comprising a titanium, a zirconium, or a hafnium atom.

[0035] The catalyst compound may comprise:

(pentamethylcyclopentadienyl)(propylcyclopentadienyl)MX_2,

(tetramethylcyclopentadienyl)(propylcyclopentadienyl)MX_2,

(tetramethylcyclopentadienyl)(butylcyclopentadienyl)MX_2,

$Me_2Si(indenyl)_2MX_2$,

$Me_2Si(tetrahydroindenyl)_2MX_2$,

(n-propyl cyclopentadienyl)$_2MX_2$,

(n-butyl cyclopentadienyl)$_2MX_2$,

(1-methyl, 3-butyl cyclopentadienyl)$_2MX_2$,

$HN(CH_2CH_2N(2,4,6\text{-}Me_3phenyl))_2MX_2$,

$HN(CH_2CH_2N(2,3,4,5,6\text{-}Me_5phenyl))_2MX_2$,

(propyl cyclopentadienyl)(tetramethylcyclopentadienyl)MX_2,

(butyl cyclopentadienyl)$_2MX_2$,

(propyl cyclopentadienyl)$_2MX_2$, and mixtures thereof,

wherein M is Zr or Hf, and X is selected from F, Cl, Br, I, Me, benzyl, CH_2SiMe_3, and C_1 to C_5 alkyls or alkenyls.

[0036] The method may comprise any one or more of the hereinbefore disclosed features in any combination.

[0037] In another aspect, there is also provided a process for polymerizing olefins, the process comprising: contacting olefins with one or more supported catalyst compositions as hereinbefore disclosed in a reactor under polymerization conditions to produce an olefin polymer or copolymer.

DETAILED DESCRIPTION

[0038] Before the present compounds, components, compositions, and/or methods are disclosed and described, it is to be understood that unless otherwise indicated this invention is not limited to specific compounds, components, compositions, reactants, reaction conditions,

CLAIMS

What is claimed is:

1. A supported olefin polymerization catalyst composition comprising one or more particulate supports, one or more catalyst compounds, a continuity additive and one or more activator compounds, wherein the supported catalyst composition is formed by drying a suspension including the one or more particulate supports, the one or more catalyst compounds, the continuity additive, the one or more activator compounds, and a diluent and has a macro pore volume, as determined by ISO 15901-1, of less than or equal to 1.23 cm^3/g but greater than or equal to 0.8 cm^3/g, wherein the drying is performed at a temperature of less than or equal to 65°C and at a pressure that is less than or equal to 8 psia; and wherein one or more catalyst compounds are metallocene type catalyst compounds and/ or conventional-type transition metal catalyst compounds.

2. A supported olefin polymerization catalyst composition according to claim 1, wherein the supported olefin polymerization catalyst composition has a macro pore volume of less than or equal to 1.23 cm^3/g but greater than or equal to 0.9 cm^3/g,

3. A supported olefin polymerization catalyst composition according to claim 1, wherein the supported catalyst composition has a macro pore volume of less than or equal to 1.20 cm^3/g, or less than or equal to 1.10 cm^3/g, or less than or equal to 1.00 cm^3/g; or
wherein the supported catalyst composition has a tapped bulk density of greater than or equal to 0.30 g/cm^3, or greater than or equal to 0.35 g/cm^3, or greater than or equal to 0.40 g/cm^3 or greater than or equal to 0.45 g/cm^3.

4. A supported olefin polymerization catalyst composition according to claim 1, wherein the particulate support is a particulate Group 2, 3, 4, 5, 13 and 14 oxide or chloride; or
wherein the particulate support is a particulate silica; or

wherein the particulate support a particulate silica having an average particle size in the range of from 0.1 to 500 μm, or from 1 to 200 μm, or from 1 to 50 μm, or from 5 to 50 μm.

5. A supported olefin polymerization catalyst composition according to claim 1, wherein the one or more activator compounds is an alumoxane or a neutral or ionic stoichiometric activator; or

wherein the supported catalyst composition has a ratio of Al/Si on the external surface area of the support to Al/Si on the internal surface area of the support is less than or equal to 3.0, or less than or equal to 2.5; or

wherein the one or more activator compounds is a methylalumoxane or modified methylalumoxane.

6. A supported olefin polymerization catalyst composition according to any one of claims 1 to 5, wherein the one or more catalyst compounds comprise a titanium, a zirconium, or a hafnium atom; or

wherein the supported catalyst composition comprises two or more catalyst compounds comprising a titanium, a zirconium, or a hafnium atom; or

wherein the catalyst compound comprises:

(pentamethylcyclopentadienyl)(propylcyclopentadienyl)MX_2,

(tetramethylcyclopentadienyl)(propylcyclopentadienyl)MX_2,

(tetramethylcyclopentadienyl)(butylcyclopentadienyl)MX_2,

$Me_2Si(indenyl)_2MX_2$,

$Me_2Si(tetrahydroindenyl)_2MX_2$,

(n-propyl cyclopentadienyl)$_2MX_2$,

(n-butyl cyclopentadienyl)$_2MX_2$,

(1-methyl, 3-butyl cyclopentadienyl)$_2MX_2$,

$HN(CH_2CH_2N(2,4,6\text{-}Me_3phenyl))_2MX_2$,

$HN(CH_2CH_2N(2,3,4,5,6\text{-}Me_5phenyl))_2MX_2$,

(propyl cyclopentadienyl)(tetramethylcyclopentadienyl)MX_2,

(butyl cyclopentadienyl)$_2MX_2$,

(propyl cyclopentadienyl)$_2MX_2$, and mixtures thereof,

wherein M is Zr or Hf, and X is selected from F, Cl, Br, I, Me, benzyl, CH_2SiMe_3, and C_1 to C_5 alkyls or alkenyls.

7. A method for producing a supported olefin polymerization catalyst composition comprising the steps of:

a) forming a suspension comprising one or more particulate supports, one or more catalyst compounds, a continuity additive, and one or more activator compounds in one or more liquid diluents; and

b) drying the suspension to form the supported catalyst composition;

wherein the supported catalyst composition has a macro pore volume, as determined by ISO 15901-1, of less than or equal to 1.23 cm^3/g but greater than or equal to 0.8 cm^3/g and step b) is performed at a temperature of less than or equal to 65°C and at a pressure which is greater than or equal to the vapor pressure of the one or more diluents, wherein the pressure is less than or equal to 8 psia; and wherein one or more catalyst compounds are metallocene type catalyst compounds and/ or conventional-type transition metal catalyst compounds.

8. A method according to claim 7 wherein the supported olefin polymerization catalyst composition has a macro pore volume of less than or equal to 1.23 cm^3/g but greater than or equal to 0.9 cm^3/g,

9. A method according to claim 7 wherein substantially no gas bubbles of diluent are formed in the pores of the support; or

wherein the drying is performed at a temperature of less than or equal to 60°C, or less than or equal to 55°C, or less than or equal to 50°C, or less than or equal to 45°C; or

wherein the drying is performed at a pressure of less than or equal to 2 psia, or less than or equal to 3 psia, or less than or equal to 4 psia, or less than or equal to 5 psia, or less than or equal to 6 psia; or

wherein the supported catalyst composition has a macro pore volume of less than or equal to 1.23 cm^3/g; or

wherein the liquid diluent comprises an aliphatic or aromatic hydrocarbon; or

wherein the liquid diluent comprises toluene.

10. A method according to any one of claims 7 to 9, wherein the supported catalyst composition has a macro pore volume of less than or equal to 1.20 cm^3/g, or less than or equal to 1.10 cm^3/g, or less than or equal to 1.00 cm^3/g; or

wherein the supported catalyst composition has a tapped bulk density of greater than or equal to 0.30 g/cm^3, or greater than or equal to 0.35 g/cm^3, or greater than or equal to 0.40 g/cm^3 or greater than or equal to 0.45 g/cm^3.

wherein the particulate support is a particulate Group 2, 3, 4, 5, 13 and 14 oxide or chloride; or
wherein the particulate support is a particulate silica; or
wherein the particulate support is a particulate silica having an average particle size in the range of from 0.1 to 500 μm, or from 1 to 200 μm, or from 1 to 50 μm, or from 5 to 50 μm.

11. A method according to any one of claims 7 to 10, wherein the one or more activator compounds is an alumoxane or a neutral or ionic stoichiometric activator; or
wherein the supported catalyst composition has a ratio of Al/Si on the external surface area of the support to Al/Si on the internal surface area of the support of less than or equal to 3.0, or less than or equal to 2.5; or
wherein the one or more activator compounds is a methylalumoxane or modified methylalumoxane; or
wherein the one or more catalyst compounds comprise a titanium, a zirconium, or a hafnium atom; or
wherein the supported catalyst composition comprises two or more catalyst compounds comprising a titanium, a zirconium, or a hafnium atom; or
wherein the catalyst compound comprises:

(pentamethylcyclopentadienyl)(propylcyclopentadienyl)MX_2,
(tetramethylcyclopentadienyl)(propylcyclopentadienyl)MX_2,
(tetramethylcyclopentadienyl)(butylcyclopentadienyl)MX_2,
$Me_2Si(indenyl)_2MX_2$,
$Me_2Si(tetrahydroindenyl)_2MX_2$,
(n-propyl cyclopentadienyl)$_2MX_2$,
(n-butyl cyclopentadienyl)$_2MX_2$,
(1-methyl, 3-butyl cyclopentadienyl)$_2MX_2$,
$HN(CH_2CH_2N(2,4,6\text{-}Me_3phenyl))_2MX_2$,
$HN(CH_2CH_2N(2,3,4,5,6\text{-}Me_5phenyl))_2MX_2$,

(propyl cyclopentadienyl)(tetramethylcyclopentadienyl)MX_2,

(butyl cyclopentadienyl)$_2MX_2$,

(propyl cyclopentadienyl)$_2MX_2$, and mixtures thereof,

wherein M is Zr or Hf, and X is selected from F, Cl, Br, I, Me, benzyl, CH_2SiMe_3, and C_1 to C_5 alkyls or alkenyls.

12. A process for polymerizing olefins, the process comprising:

contacting olefins with one or more supported catalyst compositions according to any one of claims 1 to 6 in a reactor under polymerization conditions to produce an olefin polymer or copolymer.